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STUDIES ON THE  $P$ - $V$ - $T$  RELATIONS OF FLUIDS AT HIGH PRESSURE IIThe  $P$ - $V$ - $T$  Relations of Ammonia in the Neighborhood of  
Critical Point and the Critical Values of Ammonia

BY KAORU DATE

Using the variable volume method, the  $P$ - $V$ - $T$  relations of ammonia in the neighborhood of critical point have been measured within an error of 0.2% in regard to the compressibility factor  $Z$ . Seven  $P$ - $V$  isotherms were obtained in the range of 131.05 to 133.96°C, 109.33 to 117.05 atm and 53.42 to 110.22 cc/mol around the critical point.

The critical values of ammonia were determined from the isotherms as  $T_c = 132.3^\circ\text{C}$ ,  $P_c = 111.7$  atm and  $V_c = 72.05$  cc/mol.

## Introduction

For the experimental study of the  $P$ - $V$ - $T$  relation of polar fluid, the author had already measured the  $P$ - $V$ - $T$  relation of ammonia in gaseous and liquid states at several temperatures from 25 to 125°C and at pressures up to 500 atm and reported in the previous paper<sup>1)</sup>. The experimental results for the  $P$ - $V$ - $T$  relation of ammonia were also reported in several papers by the other investigators, but there has been none in the neighborhood of its critical point. Therefore, the measurements of the  $P$ - $V$ - $T$  relation of ammonia were undertaken at several temperatures and in the pressure range from 108 to 117 atm around the critical temperature and pressure. In addition, the critical values of ammonia were determined by the use of these experimental  $P$ - $V$ - $T$  results.

## Experimental

The method and apparatus were the same as those in the measurement of the  $P$ - $V$ - $T$  relation of liquid ammonia based on the variable volume type described in detail<sup>1)</sup> in the previous paper. It was used for the sample ammonia that was prepared in the same manner as that in the previous work<sup>1)</sup> and that was believed to be above 99.9% pure. The errors for every measurement variables were 0.01% for pressure  $P$  ( $110 \pm 0.01$  atm), 0.1% for volume  $v$  ( $15 \pm 0.01$  to  $35 \pm 0.015$  cc), 0.01% for temperature  $T$  ( $400 \pm 0.05$  K) and 0.05% for mole  $n$  ( $0.3 \pm 0.00015$  mol) respectively, similar to those in

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1) K. Date, *This Journal*, **43**, 1 (1973)

the previous work<sup>1)</sup>. Then it is believed that the compressibility factors of ammonia,  $Z=Pv/nRT$ , were obtained within an error of 0.2% in maximum, estimating from the above errors for  $P$ ,  $v$ ,  $T$  and  $n$ .

### Results on $P$ - $V$ - $T$ measurement

The specific volumes of ammonia,  $V$ , were measured in the range from 53 to 110cc/mol at each corresponding pressure and at seven constant temperatures in the range of 131.05 to 133.96°C. The results are presented in Table 1 and represented graphically in Fig. 1. It is shown in Fig. 1 that each smoothed isotherm is in excellent agreement with each experimental point. Each experimental pressure at each horizontal part of the isotherm from 131.05 to 132.25°C, that is, the saturated vapor pressure, was measured to be constant respectively at each constant temperature, within a maximum fluctuation of 0.06 atm.

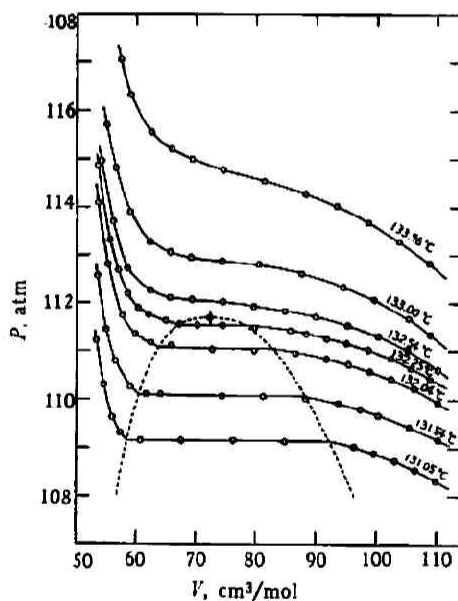


Fig. 1 Isotherms of ammonia in the neighborhood of critical point

The broken line in Fig. 1 is the line obtained to connect the points of the specific volume of saturated vapor with those of saturated liquid on the isotherms. The point represented as  $\diamond$  is the critical point of ammonia determined in the following section.

### Determination of critical values

There are several kinds of methods for the measurement of the critical values of any substances, that is, the critical temperature  $T_c$ , the critical pressure  $P_c$  and the critical specific volume  $V_c$  or the

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Table I Experimental  $P$ - $V$ - $T$  values of ammonia  
in the neighborhood of critical point

| $T$ (°C) | $1/V$ (mol/l) | $P$ (atm) | $V$ (cc/mol) | $Z$    |
|----------|---------------|-----------|--------------|--------|
| 131.05°C | 9.110         | 108.33    | 109.77       | 0.3585 |
|          | 9.396         | 108.55    | 106.43       | 0.3483 |
|          | 9.709         | 108.75    | 103.00       | 0.3377 |
|          | 10.042        | 108.89    | 99.58        | 0.3269 |
|          | 10.399        | 109.03    | 96.16        | 0.3161 |
|          | 11.784        | 109.14    | 84.86        |        |
|          | 13.114        | 109.17    | 76.25        |        |
|          | 13.114        | 109.17    | 67.71        |        |
|          | 14.768        | 109.17    | 60.85        |        |
|          | 17.420        | 109.31    | 57.41        | 0.1892 |
|          | 17.843        | 109.65    | 56.04        | 0.1852 |
|          | 18.297        | 110.32    | 54.65        | 0.1818 |
| 131.54°C | 18.720        | 111.21    | 53.42        | 0.1791 |
|          | 9.073         | 109.18    | 110.21       | 0.3623 |
|          | 9.485         | 109.44    | 105.43       | 0.3474 |
|          | 9.971         | 109.68    | 100.29       | 0.3312 |
|          | 10.286        | 109.81    | 97.22        | 0.3215 |
|          | 10.664        | 109.93    | 93.77        | 0.3104 |
|          | 11.350        | 110.03    | 88.11        |        |
|          | 12.308        | 110.07    | 81.25        |        |
|          | 13.444        | 110.09    | 74.38        |        |
|          | 15.603        | 110.13    | 64.09        |        |
|          | 16.208        | 110.12    | 61.70        |        |
|          | 16.963        | 110.27    | 58.95        | 0.1957 |
|          | 17.685        | 110.80    | 56.55        | 0.1887 |
|          | 18.127        | 111.45    | 55.17        | 0.1852 |
| 132.04°C | 18.657        | 112.56    | 53.60        | 0.1817 |
|          | 9.075         | 109.93    | 110.19       | 0.3643 |
|          | 9.406         | 110.23    | 106.32       | 0.3525 |
|          | 9.753         | 110.44    | 102.53       | 0.3406 |
|          | 10.110        | 110.59    | 98.91        | 0.3290 |
|          | 10.474        | 110.73    | 95.47        | 0.3180 |
|          | 10.903        | 110.84    | 91.72        | 0.3508 |
|          | 11.552        | 110.95    | 86.57        | 0.2889 |
|          | 12.547        | 111.00    | 79.70        |        |
|          | 13.730        | 111.04    | 72.83        |        |
|          | 15.163        | 111.12    | 65.95        |        |
|          | 15.985        | 111.17    | 62.56        | 0.2092 |
|          | 16.678        | 111.35    | 59.96        | 0.2008 |
|          | 17.319        | 111.75    | 57.74        | 0.1940 |
|          | 18.064        | 112.82    | 55.36        | 0.1878 |
|          | 18.648        | 114.10    | 53.63        | 0.1840 |

|          |        |        |        |        |
|----------|--------|--------|--------|--------|
| 132.25°C | 9.190  | 110.44 | 108.81 | 0.3612 |
|          | 9.456  | 110.65 | 105.75 | 0.3518 |
|          | 9.770  | 110.86 | 102.35 | 0.3411 |
|          | 10.141 | 111.03 | 98.61  | 0.3291 |
|          | 10.528 | 111.17 | 94.98  | 0.3174 |
|          | 10.902 | 111.26 | 91.73  | 0.3068 |
|          | 11.324 | 111.35 | 88.31  | 0.2956 |
|          | 11.654 | 111.43 | 85.81  | 0.2874 |
|          | 12.519 | 111.48 | 79.88  | 0.2677 |
|          | 13.409 | 111.54 | 74.58  |        |
|          | 14.228 | 111.55 | 70.28  |        |
|          | 14.843 | 111.56 | 67.37  |        |
|          | 15.392 | 111.64 | 64.97  | 0.2180 |
|          | 16.075 | 111.76 | 62.21  | 0.2090 |
|          | 16.578 | 111.89 | 60.32  | 0.2029 |
|          | 17.015 | 112.20 | 58.77  | 0.1982 |
|          | 17.534 | 112.69 | 57.03  | 0.1932 |
|          | 17.965 | 113.34 | 55.65  | 0.1896 |
|          | 18.654 | 114.86 | 53.61  | 0.1851 |
| 132.54°C | 9.073  | 110.60 | 110.22 | 0.3662 |
|          | 9.517  | 111.02 | 105.08 | 0.3504 |
|          | 9.972  | 111.31 | 100.28 | 0.3353 |
|          | 10.509 | 111.53 | 95.16  | 0.3188 |
|          | 11.112 | 111.72 | 89.99  | 0.3020 |
|          | 11.785 | 111.83 | 84.85  | 0.2850 |
|          | 12.547 | 111.92 | 79.70  | 0.2680 |
|          | 13.412 | 112.04 | 74.56  | 0.2509 |
|          | 14.409 | 112.08 | 69.40  | 0.2336 |
|          | 15.198 | 112.12 | 65.80  | 0.2216 |
|          | 16.032 | 112.26 | 62.38  | 0.2104 |
|          | 17.062 | 112.73 | 58.61  | 0.1985 |
|          | 17.790 | 113.70 | 56.21  | 0.1920 |
|          | 18.420 | 114.96 | 54.29  | 0.1875 |
| 133.00°C | 9.184  | 111.34 | 108.89 | 0.3638 |
|          | 9.485  | 111.66 | 105.43 | 0.3532 |
|          | 10.040 | 112.06 | 99.60  | 0.3349 |
|          | 10.586 | 112.33 | 94.46  | 0.3184 |
|          | 11.417 | 112.62 | 87.59  | 0.2960 |
|          | 12.412 | 112.82 | 80.57  | 0.2727 |
|          | 13.443 | 112.86 | 74.39  | 0.2519 |
|          | 14.443 | 112.97 | 69.23  | 0.2347 |
|          | 15.194 | 113.07 | 65.82  | 0.2233 |
|          | 16.027 | 113.29 | 62.39  | 0.2121 |
|          | 16.967 | 113.90 | 58.94  | 0.2014 |
|          | 17.688 | 114.82 | 56.54  | 0.1948 |
|          | 18.125 | 115.72 | 55.17  | 0.1916 |

|          |        |        |        |        |
|----------|--------|--------|--------|--------|
| 133.96°C | 9.196  | 112.83 | 108.74 | 0.3673 |
|          | 9.642  | 113.30 | 103.71 | 0.3517 |
|          | 10.143 | 113.70 | 98.59  | 0.3355 |
|          | 10.704 | 114.03 | 93.42  | 0.3189 |
|          | 11.329 | 114.28 | 88.27  | 0.3020 |
|          | 12.281 | 114.55 | 81.43  | 0.2792 |
|          | 13.410 | 114.78 | 74.57  | 0.2562 |
|          | 14.410 | 114.99 | 69.40  | 0.2389 |
|          | 15.158 | 115.21 | 65.97  | 0.2275 |
|          | 15.989 | 115.56 | 62.54  | 0.2163 |
|          | 16.917 | 116.33 | 59.11  | 0.2058 |
|          | 17.419 | 117.05 | 57.41  | 0.2012 |

critical density  $1/V_c$ . Among the methods, there is one using the  $P$ - $V$ - $T$  relations in the neighborhood of the critical point.

Since the critical point can be defined as the position at which  $(dP/dV)_T=0$  and  $(d^2P/dV^2)_T=0$  at  $T=T_c$ , the determination of the critical values of ammonia was tried by the use of the above definition and the experimental  $P$ - $V$ - $T$  values in this work, as follows.

For  $T_c$ , the minimum values of  $(dP/dV)_T$  at each isotherm,  $(dP/dV)_{T, \min}$ , were estimated graphically and they were plotted against  $T$  as shown in Fig. 2. The  $T_c$  value was obtained as  $132.33 \pm 0.05^\circ\text{C}$  extrapolating the line in Fig. 2 to  $(dP/dV)_{T, \min}=0$ . As shown in Fig. 3, the  $P_c$  value was also obtained as  $111.65 \pm 0.05 \text{ atm}$  in a similar manner as above for  $T_c$ . Nevertheless, the  $V_c$  value could not be obtained so clearly by the use of the extrapolation of  $(dP/dV)_{T, \min}$  to 0 in the graph of  $(dP/dV)_{T, \min}$  vs.  $V$ , in a similar manner as above for  $T_c$  and  $P_c$ , that it lay in the range of about 70 to 75 cc/mol.

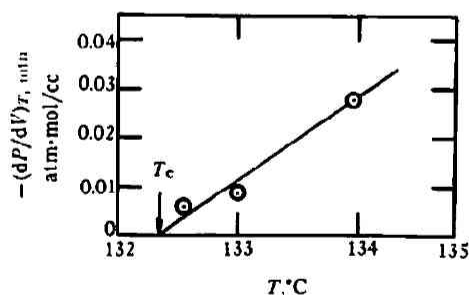


Fig. 2  $(dP/dV)_{T, \min}$  vs. temperature curve

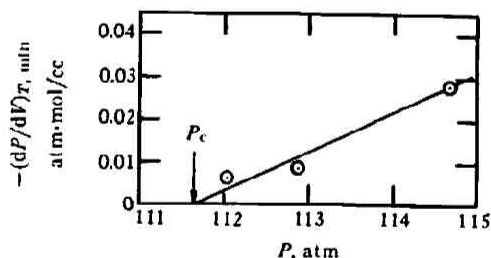


Fig. 3  $(dP/dV)_{T, \min}$  vs. pressure curve

On the other hand, there had been presented the method to determine the value of  $V_c$  very accurately by the use of the law of rectilinear diameters proposed by Cailletet and Mathias. This law claims that the arithmetical mean of the saturated liquid density  $1/V_l$  and the saturated vapor density  $1/V_g$  both at the same temperature,  $(1/2)[(1/V_l) + (1/V_g)]_T$ , decrease linearly to the critical point with the increase of temperature. It is only empirical but it has been confirmed since olden times that the law is applicable to many substances. According to this law, the value of  $1/V_c$  can be easily deter-

mined as the value of  $1/V$  at the point of intersection of two curves, that is, one is the straight line of  $(1/2)[(1/V_l) + (1/V_g)]$  and the other is the curve connecting  $1/V_l$  and  $1/V_g$  lines smoothly, in the graph of  $1/V$  vs.  $T$ . Using this method and the experimental values of density given in Table 2, the critical value was finally determined as  $1/V_c = 13.88 \pm 0.03 \text{ mol/l} = 0.2364 \pm 0.0005 \text{ g/cc}$  or  $V_c = 72.05 \pm 0.08 \text{ cc/mol}$ . It is also shown in Fig. 4.

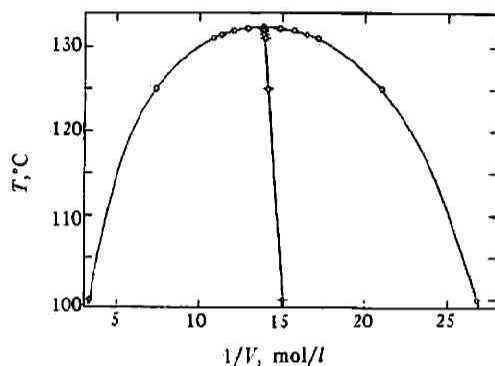


Fig. 4 Law of rectilinear diameters for ammonia

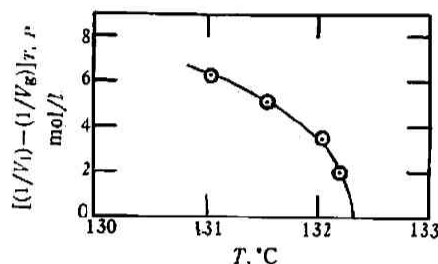
Fig. 5  $[(1/V_l) - (1/V_g)]_{T,P}$  vs. temperature curve

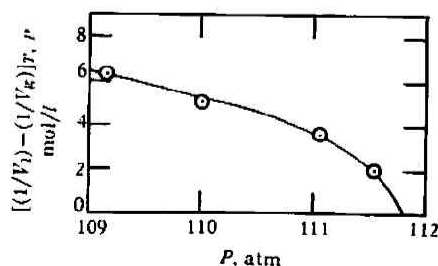
Table 2 Experimental values of saturated vapor pressure, saturated vapor density and saturated liquid density of ammonia

| Temp.<br>$t$ ( $^{\circ}\text{C}$ ) | Saturated vapor<br>pressure,<br>$P$ (atm) | Saturated vapor<br>density,<br>$1/V_g$ (mol/l) | Saturated liquid<br>density,<br>$1/V_l$ (mol/l) |
|-------------------------------------|---|--|---|
| 100                                 | 61.65*                                    | 3.30**   | 26.81*  |
| 125                                 | 98.15*                                    | 7.34**   | 21.00*  |
| 131.05                              | 109.16                                    | 10.84  | 17.15   |
| 131.54                              | 110.09                                    | 11.32  | 16.47   |
| 132.04                              | 111.06                                    | 12.08  | 15.71   |
| 132.25                              | 111.55                                    | 12.81  | 14.84   |

\* These are the experimental values in previous work<sup>1)</sup>.

\*\* These are the extrapolated values of the experimental densities of gaseous ammonia in previous work<sup>1)</sup> to the saturated vapor pressures.

To prove the validity for the values of  $T_c$  and  $P_c$  obtained above, an examination was done as follows.

Fig. 6  $[(1/V_l) - (1/V_g)]_{T,P}$  vs. pressure curve

Since it is expected that the limit values of  $1/V_l$  and  $1/V_g$  to the critical point are to be equal, the experimental  $[(1/V_l) - (1/V_g)]T, P$  values were plotted against  $T$  or  $P$  in graph and the curve was extrapolated through the experimental points to zero. Then the value of  $T$  or  $P$  at  $[(1/V_l) - (1/V_g)]T, P = 0$  was obtained as  $132.38^\circ\text{C}$  or  $111.84\text{ atm}$  respectively which corresponded very nearly to the value of  $T_c$  or  $P_c$  mentioned above. These figures are shown in Fig. 5 and 6.

Finally, for the most probable critical values of ammonia, they were determined as  $T_c = 132.3^\circ\text{C}$ ,  $P_c = 111.7\text{ atm}$ ,  $V_c = 72.0\text{ cc/mol}$  or  $1/V_c = 0.2364\text{ g/cc}$  and the critical compressibility factor  $Z_c = P_c V_c / RT_c = 0.242$ , respectively in this work.

Table 3 Comparison of critical constants of ammonia

| Year            | $T_c$<br>( $^\circ\text{C}$ ) | $P_c$<br>(atm) | $1/V_c$<br>(g/cc) | Method* | Investigators            |
|-----------------|-------------------------------|----------------|-------------------|---------|--------------------------|
| 1884            | 130.0                         | 115.0          |                   | ?       | J. Dewar                 |
| 1886            | 131.0                         | 113.0          |                   | (1)     | C. Vincent <i>et al.</i> |
| 1903            | 132.53                        |                |                   | (1)     | M. Centnerswer           |
| 1904            |                               |                | 0.239             | (2)     | E. Mathias               |
| 1908            | 132.3                         |                |                   | (1)     | Jacquerod                |
| 1910            | 132.1                         | 111.3          |                   | (1)     | F. Scheffer              |
| 1912            | 132.9                         | 112.3          |                   | (1)     | E. Cardoso <i>et al.</i> |
| 1913            | 132.3                         |                |                   | (1)     | Estreier <i>et al.</i>   |
| 1918            | 132.3                         |                | 0.2364            | (1, 2)  | A. Berthoud              |
| 1918            | 132.3                         |                | 0.2362            | (1, 2)  | A. Berthoud              |
| 1920            | 132.35                        | 111.3          |                   | (1)     | Postma                   |
| 1923            |                               |                | 0.234             | (2)     | Cregoe <i>et al.</i>     |
| Values selected | 132.3                         | 111.3          | 0.235             | .....   | K. Kobe <i>et al.</i>    |
| This work       | 132.3                         | 111.7          | 0.2364            | (2, 3)  |                          |

\* (1) Disappearance of the meniscus

(2) Law of rectilinear diameters

(3) Pressure-volume-temperature relations;  $(dP/dV)_{T, \text{min}} = 0$

Kobe *et al.*<sup>2)</sup> had presented the most probable critical values for many substances based on the experimental values by various workers and methods. The critical values of ammonia measured by other investigators and recommended by Kobe *et al.* are presented in Table 3 together with the values determined in this work for comparison.

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2) K. A. Kobe and R. E. Lynn, Jr., *Chem. Rev.*, **52**, 117 (1953)